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XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ON THE ACTION OF SODIUM MALONIC ESTER ON TRIBROMDINITROBENZOL.

SECOND PAPER.

By C. Loring Jackson and W. S. Robinson.

Presented May 28, 1889.

In a previous paper * on this subject we were obliged to publish several results in an unfinished condition, because at the time we saw no chance of being able to continue the work together. Since then, however, unforeseen circumstances have allowed us to go on with the research, and in this paper we describe work which fills up most of the gaps in our former publication.

The most important results contained in this paper may be stated briefly as follows. The reactions by which the bromdinitrophenylmalonic ester is formed have been made out to be the following: —

I. $C_6HBr_3(NO_2)_2 + CHNa(COOC_2H_5)_2 =$
$NaBr + C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2$.

II. $C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + CHNa(COOC_2H_5)_2 =$
$C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2$.

III. $C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2$.

IV. $CHNa(COOC_2H_5)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2$.

V. $CHBr(COOC_2H_5)_2 + NaOH = NaBr + CHOH(COOC_2H_5)_2$.

The proof of these reactions consisted in the isolation of tartronic acid from the mixture obtained by the saponification of the oily secondary product with hydrochloric acid.

The action of concentrated hydrochloric acid, or, better, sulphuric acid of specific gravity 1.44, upon the bromdinitrophenylmalonic ester

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* These Proceedings, xxiv. 1.

has been studied, and we are able to correct some of the preliminary statements made on this subject in our first paper. The product is the bromdinitrophenylacetic acid

$$C_6H_2Br(NO_2)_2CH_2COOH,$$

which melts at 177°, and is formed, when hydrochloric acid is used, by the following reactions: —

$$\begin{aligned} &C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2 + 2\,HCl = \\ &\quad 2\,C_2H_5Cl + C_6H_2Br(NO_2)_2CH(COOH)_2 = \\ &\quad 2\,C_2H_5Cl + CO_2 + C_6H_2Br(NO_2)_2CH_2COOH. \end{aligned}$$

The crystalline silver salt of this acid was analyzed, and proved to have the formula

$$C_6H_2Br(NO_2)_2CH_2COOAg\,.\,H_2O.$$

With sodic hydrate a deep Prussian green or with an excess a yellowish brown solution is formed, from which acids throw down a pale crimson precipitate, or a white one which becomes pale crimson when moistened with alcohol; none of these substances could be brought into a state fit for analysis, but we found that bromine was removed in their formation.

The bromdinitrophenylacetic acid is broken up when boiled with alcohol into bromdinitrotoluol and carbonic dioxide; boiling with water produces the same effect, but much more slowly. A few drops of sulphuric acid prevent the decomposition by boiling water. This conversion into bromdinitrotoluol gave us the means of determining the constitution of the bromdinitrophenylmalonic ester and its derivatives; as Messrs. W. B. Bentley and W. H. Warren have, at our request, worked out the constitution of the substituted toluol, and found that it is as follows:

$$CH_3\,.\,Br\,.\,NO_2\,.\,NO_2\,.\,1\,.\,3\,.\,4\,.\,6.$$

It follows, therefore, that all the substances mentioned in this and our former paper must have a similar constitution, and that in making the bromdinitrophenylmalonic ester from bromdinitrobenzol the bromine atom replaced by the malonic radical is one of those which is at the same time para and ortho to the nitro groups, the one replaced by hydrogen is ortho to the two nitro groups, while the third atom of bromine, which remains unaltered, occupies exactly the same position as that replaced by the malonic ester radical, — certainly a curious result.

Preparation of Bromdinitrophenylmalonic Ester.

Our longer experience in the preparation of bromdinitrophenylmalonic ester has led us to introduce several improvements into the process, which now we carry on as follows. A strong benzol solution of 20 grs. of tribromdinitrobenzol (benzol is to be preferred to the ether used formerly, because the tribromdinitrobenzol is more soluble in it) is mixed with 16 grs. of malonic ester previously converted into sodium malonic ester by treatment with the sodic ethylate from 2.3 grs. of sodium and about 100 to 125 c.c. of alcohol, and the mixture allowed to stand over night at ordinary temperatures. The red solution thus obtained is treated with water, which separates it into two layers, a dark red aqueous solution containing the sodium salt of bromdinitrophenylmalonic ester and sodic bromide, and a benzol solution of the unaltered tribromdinitrobenzol with the oily product of the reaction. The two layers are separated with a drop-funnel, and the lower aqueous one acidified with dilute sulphuric acid; this throws down a yellowish white precipitate of the bromdinitrophenylmalonic ester, which is purified by crystallization from hot alcohol, until it shows the constant melting point 76°.

In this way 20 grs. of tribromdinitrobenzol gave 7.9 grs. of the bromdinitrophenylmalonic ester,* and 5.1 grs. of tribromdinitrobenzol were recovered from the benzol solution. Subtracting this from the 20 grs. there are left 14.9 grs. of tribromdinitrobenzol, which entered into the reaction, and should have given the same weight, 14.9 grs., of the product, so that the yield was 53 per cent of the theory, or about the same as that obtained by the process as given in our first paper, which calculated in the same way becomes 50 per cent.

In the course of some other experiments the curious observation was made that it is not necessary to use sodic ethylate to bring about the action of malonic ester on the tribromdinitrobenzol, as a little of the red salt of bromdinitrophenylmalonic ester was formed when *aqueous* sodic hydrate was added to a mixture of the two organic substances. This recalls the observation of Victor Meyer,* that homologues can be obtained from benzylcyanide by using the alkylhaloid with powdered solid sodic hydrate instead of sodic ethylate, or from desoxybenzoin by the use of an alcoholic solution of an alkaline hydrate.

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* Dr. G. D. Moore, in his work with me on the action of sodium acetacetic ester on tribromdinitrobenzol, has found that a much better yield is obtained if the mixture is boiled for an hour under a return condenser. This observation was not made until the work described in this paper was finished and Mr. Robinson had left Cambridge, so that it was not convenient to try the experiment of boiling the solution of sodium malonic ester and tribromdinitrobenzol, nor did it seem very desirable to do so, as when we first took up the subject such an experiment was tried, and seemed to yield very unfavorable results. I propose, however, to repeat the experiment next year, if I return to the study of these compounds. C. L. J.

Study of the Reactions by which the Bromdinitrophenylmalonic Ester is formed.

One of the most important points, which want of time prevented us from considering in our first paper, was the mechanism of the reactions by which the bromdinitrophenylmalonic ester was formed from the tribromdinitrobenzol, and accordingly this was one of the first points to which we turned our attention in taking up the subject again. The reaction consists essentially, as our analyses of the product showed, in the replacement of one of the bromine atoms in the tribromdinitrobenzol by the malonic ester radical $CH(COOC_2H_5)_2$, and of a second by hydrogen forming $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$, and the obscure part of it is the manner in which this second atom of bromine is replaced by hydrogen. The first step toward clearing up this obscurity was obviously to make out whether this atom of bromine was eliminated in the form of some organic compound, or as sodic bromide, which was done by the following quantitative determinations of the amount of sodic bromide formed in the reaction.

I. 20 grs. of tribromdinitrobenzol were treated with the sodium malonic ester from 16 grs. of malonic ester in the way already described, and, after precipitating the bromdinitrophenylmalonic ester from the aqueous solution with dilute nitric acid, and filtering it out, the amount of sodic bromide was determined by precipitation of argentic bromide from an aliquot part of the filtrate, and calculating the amount in the entire solution. In this way the whole solution was found to yield 13.81 grs. of argentic bromide, corresponding to 5.88 grs. of bromine. The benzol solution on evaporation yielded 5.1 grs. of tribromdinitrobenzol, which had not taken part in the reaction, leaving 14.9 grs. which had acted, and which would yield 5.89 grs. of bromine, if two of the atoms of bromine had been removed from each molecule as sodic bromide.

II. 20 grs. of tribromdinitrobenzol gave under the same conditions 13.8 grs. of argentic bromide corresponding to 5.87 grs. of bromine, but only 4.9 grs. of tribromdinitrobenzol were recovered unaltered.

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* Ber. d. ch. G. 1888, p. 1291.

The 15.1 grs. of tribromdinitrobenzol which entered into the reaction should have lost 5.96 grs. of bromine.

Percentage of the theoretical amount of bromine removed from tribromdinitrobenzol in the form of sodic bromide: —

I.	II.
99.86	98.49

These numbers agree as closely as could be expected, when the necessary sources of error in the process are considered, and prove that all the bromine removed by the reaction is converted into sodic bromide.

The second point to be determined was from what source the atom of hydrogen was obtained which replaced the atom of bromine. For this purpose we investigated the oily product of the reaction, and, after we had found that nothing definite could be obtained from it by distillation under ordinary pressures, or with steam, and that sodic hydrate or other alkaline saponifying agents gave most unpromising results, we tried heating it with strong hydrochloric acid in a sealed tube to 130° for 20 hours, as the bromdinitrophenylmalonic ester which was dissolved in the oil would be converted by this treatment into the corresponding phenylacetic acid, with the properties of which we were familiar, and which therefore we thought could be removed easily from the other products of the reaction. The tubes after heating contained an aqueous solution and a small amount of viscous matter, which gradually changed into an amorphous solid. These were separated by filtration, and the filtrate evaporated to dryness on the water bath, leaving a crystalline residue, which was extracted with cold water to leave behind the bromdinitrophenylacetic acid present. The extract after being evaporated again on the water bath gave crystals, which made up about one half the amount of the residue from the first evaporation. They were freely soluble in water or alcohol, nearly insoluble in ether, and could be sublimed at temperatures below their melting point forming glassy white thick needles or prisms, which melted at 185°. These properties prove that the crystals are tartronic acid, as they are identical with those given by Conrad and Bischoff for that substance.* We tried also to confirm this inference by an analysis, but the small amount of the acid which after some unsuccessful experiments remained at our disposal, little more than 0.1 gr., prevented us from purifying it thoroughly, as sublimation, which had given the substance melting at 185°, turned out to be too wasteful a process for working up large amounts; we were not surprised, therefore, that our analysis of the silver salt gave 62.82 per cent of silver, instead of the 64.69 per cent calculated for argentic tartronate. This result, however, bad as it is, comes nearer to that for argentic tartronate than to that for any other substance which could well be formed, and therefore gives us the desired confirmation.* The small amount of tartronic acid obtained, less than 0.5 gr. from about 10 grs. of the oil, may be accounted for on the supposition that the larger part of the tartronic acid was decomposed by the strong hydrochloric acid used in the saponification of the oil, as Conrad and Bischoff† have observed that tartronic acid is decomposed very easily by hydrochloric acid, and we also were unable to obtain a trace of the acid from the filtrate after argentic chloride had been precipitated from the silver salt by a slight excess of hydrochloric acid. In fact, we should not have thought it worth while to try to obtain tartronic acid by the action of hydrochloric acid on our oil, if it had not been for the fact that tartronic ester has been made from calcic tartronate by the action of hydrochloric acid gas and alcohol,‡ which would seem to show that the tartronic acid is more stable in presence of strong than of dilute hydrochloric acid, improbable as this sounds. This view is in harmony with our observations detailed above, and Conrad and Bischoff state that even very dilute acid decomposes it readily; but even granting this, a large proportion of the tartronic acid must have been decomposed during the treatment with hydrochloric acid, and this seems to us sufficient to make it more than probable that the tartronic acid is the product of the principal reaction, and not formed in a secondary one taking place only to a limited extent. If this is admitted, the following reactions would give the most probable explanation of what takes place.

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* Ann. Chem., ccix. 222.

$$\text{I.}\quad C_6HBr_3(NO_2)_2 + NaCH(COOC_2H_5)_2 = C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaBr.$$

$$\text{II.}\quad C_6HBr_2(NO_2)_2CH(COOC_2H_5)_2 + NaCH(COOC_2H_5)_2 = C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2.$$

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* No attempt was made to obtain a better analysis of the tartronic acid, because the work upon the corresponding trinitro compound described in another paper furnished a complete confirmation of the theory of the reactions given here.

† Ann. Chem., ccix. 223.

‡ Freund, Ber. d. ch. G., xvii. 786. Pinner, Ibid., xviii. 757.

III. $C_6HBr_2(NO_2)_2CNa(COOC_2H_5)_2 + CH_2(COOC_2H_5)_2 =$
$C_6H_2Br(NO_2)_2CNa(COOC_2H_5)_2 + CHBr(COOC_2H_5)_2$.

IV. $NaCH(COOC_2H_5)_2 + H_2O = NaOH + CH_2(COOC_2H_5)_2$.

V. $CHBr(COOC_2H_5)_2 + NaOH = CHOH(COOC_2H_5)_2 + NaBr$.

Of these reactions, I., II., and III. take place before, IV. and V. after, the addition of the water used in working up the product. That Reaction III. takes place we infer from our discovery of tartronic acid among the products of saponification of the oil, as Conrad and Bischoff * have proved that brommalonic ester is decomposed by sodic hydrate, according to Reaction V.†

The experiments of one of us with G. D. Moore upon the action of sodium malonic ester on tribromtrinitrobenzol have shown that these reactions take place in a way analogous to that just worked out. For the details we would refer to the paper on this subject.

The objection which might be raised against these reactions, that the yield of bromdinitrophenylmalonic ester is at best only about 50 per cent of that required by theory, and therefore that some other substance may be formed from the tribromdinitrobenzol in addition to it, is disposed of by the fact that on making the dibromdinitrophenylmalonic ester from tetrabromdinitrobenzol by exactly analogous reactions, the yield rose to 80 per cent of the theoretical.‡ It follows, therefore, that the 47 to 50 per cent unaccounted for in our preparations remained dissolved in the oily secondary product; but although we have made many attempts to recover it, none of them have been crowned with success.

The absence of malonic acid in the product of the action of hydrochloric acid on the oil seems to us extraordinary, as we purposely kept the temperature of the saponification at 130°, in order to avoid decomposing the malonic acid, which we expected from the excess of malonic ester undoubtedly present in the oil. We can account for this only by supposing that malonic acid is decomposed in presence of strong hydrochloric acid at a lower temperature than when heated alone.

Saponification of Bromdinitrophenylmalonic Ester.

In our previous paper we stated that strong hydrochloric acid decomposed bromdinitrophenylmalonic ester, when the two substances were heated together to 140°–145° in a sealed tube, and described the product formed, stating, however, that all our results up to that time must be regarded as preliminary. Upon taking up the subject again, we studied in the first place the gas evolved when the tube was opened, and found that, in addition to the gas already mentioned burning with a green-bordered flame (which is undoubtedly ethylchloride), carbonic dioxide was given off, as was proved by the precipitate formed when the gas was passed through lime-water. It is to be observed, however, that if the temperature to which the tubes were heated was 140°, or a little lower, very little, if any, carbonic dioxide was given off, and the product insoluble in the hydrochloric acid was oily; on the other hand, when a crystalline product was obtained at a somewhat higher temperature, carbonic dioxide was given off freely. We next attempted to prepare the substance in open vessels by substituting for strong hydrochloric acid dilute sulphuric acid boiling at about the temperature to which we heated the tubes, and found that not only did we obtain the product in this way, but that it was much purer than that made in the sealed tubes with hydrochloric acid. We have arrived accordingly at the following method as the most convenient for saponifying the bromdinitrophenylmalonic ester. 2 grs. of the ester are mixed with about 100 c.c. of dilute sulphuric acid, specific gravity 1.44 and boiling point 132°, and the mixture boiled in a flask with a return condenser, until the oily drops of melted bromdinitrophenylmalonic ester have all gone into solution, which usually takes about an hour and a half. After this the solution, as it cools, deposits long, pale yellow needles of the new substance, which, if the preparation has succeeded well, melt at 177° at once. If, however, the action has not run so well, and the melting point is somewhat lower than this, the substance can be easily purified by crystallization from boiling water acidified with a few drops of dilute sulphuric acid, but in no case should it be crystallized from pure water, or alcohol, as these solvents decompose it in the curious way described later in this paper, when we consider its properties.

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* Ann. Chem., ccix. 222.

† A fuller discussion of these reactions will be found in the general paper at the end of this series.

‡ These Proceedings, xxiv. 295.

Metabromdinitrophenylacetic Acid, $C_6H_2Br(NO_2)_2CH_2COOH$.

The substance prepared in the manner just described, and showing the constant melting point 177°, was dried at 100°, and analyzed with the following results: —

I. 0.2106 gr. of the substance gave on combustion 0.2426 gr. of carbonic dioxide, and 0.0420 gr. of water.

II. 0.1933 gr. of the substance gave 15.6 c.c. of nitrogen at a temperature of 15°.5, and a pressure of 759.2 mm.

III. 0.1821 gr. of the substance gave, according to the method of Carius, 0.1152 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2H$.	Found. I.	II.	III.
Carbon	31.47	31.43		
Hydrogen	1.64	2.21		
Nitrogen	9.18		9.42	
Bromine	26.23			26.93

These analyses supersede those already published,* which were made with a substance prepared by crystallization from dilute alcohol, before we had found that this solvent decomposed the compound; it was therefore decidedly impure, as indeed was shown by its melting point, which was 170° instead of 177°.

The yield of the bromdinitrophenylacetic acid is essentially quantitative, as 2 grs. of the bromdinitrophenylmalonic ester gave, after treatment with dilute sulphuric acid, 1.4 grs. of bromdinitrophenylacetic acid melting at 177°, instead of the calculated amount, 1.56 grs., that is, 90 per cent of the theory; the missing 10 per cent without doubt remained dissolved in the dilute sulphuric acid, in which the substituted acetic acid is not wholly insoluble, as the 1.4 grs. were obtained by simple filtration, no attempt being made to recover the organic substance from the filtrate.

In view of the observations described above, there can be no doubt that the following reactions take place when bromdinitrophenylmalonic ester is saponified by heating it with hydrochloric acid at temperatures in the neighborhood of 145°:

$$\begin{aligned} &C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2 + 2\,HCl = \\ &\quad C_6H_2Br(NO_2)_2CH(COOH)_2 + 2\,C_2H_5Cl = \\ &\quad C_6H_2Br(NO_2)_2CH_2COOH + CO_2 + 2\,C_2H_5Cl. \end{aligned}$$

And there can be no question that a similar reaction takes place when dilute sulphuric acid is substituted for strong hydrochloric acid. In fact, this was so obvious that we have not thought it worth while to try to isolate the sulphovinic acid which must be formed in this case instead of the ethylchloride.

Properties. — The metabromdinitrophenylacetic acid crystallizes from an aqueous solution containing a little sulphuric acid in yellowish white needles, often one to two centimeters long, which appear under the microscope as tolerably thick prisms frequently tapering owing to modification by the planes of a pyramid with a very acute angle, but almost always, even in addition to this tapering, terminated bluntly by the planes of another very obtuse pyramid. Occasionally the termination is a single plane at a moderately acute angle to the sides, but this looked as if it were due to cleavage. The crystals are generally very well developed, but if they are small, a tendency to twin longitudinally is observed. If the substance is crystallized from alcohol, the forms like feathers, or half-feathers, described in our previous paper, and groups of branching needles looking like certain feathery seaweeds, appear; but as the alcohol decomposes the substance, these forms can hardly be ascribed to the substituted acetic acid itself. It melts at 177° ; and is essentially insoluble in ligroine or carbonic disulphide; very slightly soluble in chloroform, slightly in benzol, more soluble in both of these solvents when hot; tolerably soluble in ether, separating from the solution in a liquid form, which solidifies on stirring; easily soluble in acetone or glacial acetic acid; soluble in cold alcohol, more freely in hot, but the alcohol decomposes it, as is indicated by the change in the appearance of the crystals, the long yellowish prisms of unaltered bromdinitrophenylacetic acid becoming roughly studded with fine needles of another substance, and by the lowering of the melting point, when the substance is crystallized from alcohol; evaporation to dryness of the alcoholic solution, if repeated three times, reducing the melting point from 177° to 147°; while after two more evaporations, making five in all, the melting point had sunk to 103°–104°, at which point it remained constant after repeated crystallization. The substance obtained in this way crystallized in rectangular prisms, or plates, was not acted on by alkalies, and was recognized as Grete's metabromdinitrotoluol.* For greater certainty it was analyzed, with the following results: —

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* These Proceedings, xxiv. 11.

I. 0.1690 gr. of the substance gave by the method of Carius 0.1210 gr. of argentic bromide.

II. 0.2185 gr. of the substance gave 20.3 c.c. of nitrogen at a temperature of 22°.5 and a pressure of 773.3 mm.

	Calculated for $C_6H_2Br(NO_2)_2CH_3$.	Found.	
		I.	II.
Bromine	30.65	30.47	
Nitrogen	10.73		10.69

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* Ann. Chem., clxxvii. 258.

This conversion of the metabromdinitrophenylacetic acid into the corresponding toluol by boiling with alcohol, when it is so stable in presence of boiling dilute sulphuric acid, seemed to us so interesting that we have examined it more carefully. Having in the first place determined that the alcohol was neutral to test papers, to prove that the reaction could not be due to a trace of alkali, or acid in it, a quantity of the substance melting at 177° was boiled in a flask under a return condenser with a little alcohol for three hours, and pure air occasionally drawn through the apparatus to sweep out its contents into a set of absorption bulbs filled with lime-water; in this way a heavy precipitate was obtained, which consisted in great part of calcic hydrate precipitated by the alcohol vapor, but also contained calcic carbonate, as was shown by effervescence when it was dissolved in an acid, thus proving that carbonic dioxide had been given off. The alcoholic solution, after it had been boiled for an hour and a half longer, gave crystals, melting at 103° to 104°. It seems evident, therefore, that the reaction runs as follows,

$$C_6H_2Br(NO_2)_2CH_2COOH = C_6H_2Br(NO_2)_2CH_3+CO_2,$$

and the alcohol seems to take no part in it. Methyl alcohol, in which the substance is more soluble than in ethyl alcohol, brings about a similar decomposition, but more slowly. In boiling water the metabromdinitrophenylacetic acid is tolerably soluble, but nearly insoluble in cold water. The decomposition produced by alcohol also takes place when the aqueous solution is boiled, but very slowly, so that long boiling is necessary to convert the substance completely into the substituted toluol; nevertheless, after distilling with steam for several hours, the whole of the substance had passed over into the receiver as metabromdinitrotoluol, since none of the substituted acetic acid, which does not distil with steam, was left in the flask. The presence of a very small amount of sulphuric acid (two or three drops of the dilute acid to 100 c.c. of water) is sufficient to prevent this decomposition entirely, as a specimen of the substituted acetic acid showed no signs of decomposition, even after having been distilled with steam for three hours with only the amount of dilute sulphuric acid which remained adhering to it after the excess of acid used in its preparation had been removed by filtration. The best solvent for the bromdinitrophenylacetic acid therefore is boiling water containing a few drops of sulphuric acid. If the substance has become contaminated with the substituted toluol, it can be purified conveniently by distillation with steam in presence of a few drops of sulphuric acid, when the toluol passes over, and the acetic acid remains behind in the flask.

Ammonic hydrate dissolves the metabromdinitrophenylacetic acid, forming a colorless solution if the acid is in excess; but if the ammonic hydrate is added in slight excess, a green solution is obtained, which turns dark brown if a large excess of ammonic hydrate is added, but regains its green color on dilution with water. Both the colorless and green solutions smell of ammonia, and this smell could not be removed by gentle boiling, or by allowing the solution to stand over sulphuric acid, from which we infer that the ammonium salt is a decidedly unstable substance. When either solution is warmed on the water bath for some time it is partially decomposed with formation of a precipitate of metabromdinitrotoluol, and the green solution turns yellow even when allowed to evaporate spontaneously. Hydrochloric acid threw down from the solution a precipitate of metabromdinitrophenylacetic acid. The ammoniacal solution, prepared with an excess of the acid and freed as completely as possible from an excess of ammonia, gave no precipitate with baric, strontic, or calcic chloride, but with the salts of many of the heavy metals it gave precipitates, of which the following were the most characteristic: —

Aluminic chloride, heavy, white.

Ferric chloride, heavy, very pale bluff.

Cupric sulphate, heavy, pale blue.

Mercuric nitrate, heavy, yellowish white.

Mercuric chloride, a very slight precipitate, probably white precipitate from the slight excess of ammonic hydrate.

Mercurous nitrate, heavy, white.

Plumbic acetate, heavy, white.

Argentic nitrate, heavy, white.

The behavior with argentic nitrate is especially characteristic; if the solutions are strong, the mixture becomes nearly solid from the formation of a white flocculent precipitate, which frequently swells up, forming a little heap or pyramid, and after standing for some hours becomes converted into good-sized crystals. The analysis and properties of this salt are described more in detail below.

With sodic hydrate a solution of the acid turns a deep Prussian green color, which passes in time into a yellowish brown, this latter color appearing at once when an excess of sodic hydrate is added. If the green solution is acidified, a precipitate is obtained, which, although nearly colorless when dry, becomes purple when moistened with alcohol. This precipitate was oily at first, and, although it solidified later, we did not succeed in finding any solvent from which it could be crystallized. That the sodic hydrate had acted on the bromine was shown by an actual experiment, which gave the following results.

0.67 gr. of the acid yielded by treatment with sodic hydrate so as to form the green salt 0.1136 gr. of argentic bromide, which corresponds to 0.0483 gr. of bromine instead of the 0.1757 gr. contained in the amount of acid taken; that is, 27.5 per cent of the whole had been removed.

The yellowish brown solution obtained, when a large excess of sodic hydrate was used, or the mixture of sodic hydrate and metabromdinitrophenylacetic acid was boiled for some time, gave on addition of an acid a viscous red substance, which was exceedingly unmanageable. That bromine was removed in quantity in this way is shown by the following determination.

0.2412 gr. of the metabromdinitrophenylacetic acid was boiled with sodic hydrate for three quarters of an hour; the product, after acidifying with nitric acid, and filtering out the precipitate, gave 0.1180 gr. of argentic bromide, corresponding to 0.0502 gr. of bromine instead of the 0.0632 gr. contained in the weight of acid taken; that is, 79.4 per cent of the whole.

It is evident, therefore, that the original compound has undergone a deep-seated alteration, and the new crimson substance is probably a phenol. This view of its nature receives some confirmation from the fact that it is decomposed with the greatest ease by even somewhat dilute nitric acid. We have not yet succeeded in bringing either of the products derived from sodic hydrate into a state fit for analysis, although the slight solubility of the barium salt of the crimson acid awakened hopes of success; but these ended in disappointment, as the salt proved quite as viscous as the free acid.

Potassic carbonate gives with the metabromdinitrophenylacetic acid results similar to those obtained with sodic hydrate, but less marked.

We hoped to be able to throw some light on this action of alkalies on the metabromdinitrophenylacetic acid by the study of the corresponding anilido compound, but have not succeeded as yet in preparing it, as aniline converts the free acid direct into metanilidodinitrotoluol,* $C_6H_2CH_3(C_6H_5NH)(NO_2)_2$, melting point 142°, and the saponification of anilidodinitrophenylmalonic ester with sulphuric acid yielded only uninviting viscous products.

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* Hepp, Ann. Chem., ccxv. 371.

Radziszewski,* Gabriel and R. Meyer,† and Heckmann,‡ have prepared a dinitrophenylacetic acid which differs from that just described only in containing no bromine. This substance also loses carbonic dioxide easily, passing into dinitrotoluol, but none of the chemists who have worked with it describe a decomposition by solvents similar to that observed by us; in fact, they crystallized it for analysis from boiling water, but, as in all their methods of preparation acids were used, it is possible that a sufficient amount of sulphuric acid was present during the crystallization to prevent the decomposition. It appears that none of them tried to crystallize it from alcohol. The statement is made, however, that the sodium or potassium salt of the acid decomposes slowly on standing, instantly on boiling giving carbonate and dinitrotoluol; from this it would seem probable that our bromine acid was more stable than that containing no bromine, as our ammonium salt (the sodium or potassium salt could not be obtained) stood unaltered for many days, and even could be warmed on the water bath for some minutes with only slight decomposition. The curious change of color with sodic hydrate observed by us did not occur with the dinitro body, confirming our conclusion that this action was due to the removal of bromine by the sodic hydrate.

Argentic Metabromdinitrophenylacetate,
$C_6H_2Br(NO_2)_2CH_2COOAg . H_2O$.

This substance was prepared by adding a solution of argentic nitrate to a solution of the acid in ammonic hydrate, which had been freed from the excess of ammonia as completely as possible, best by using an excess of the acid in preparing the salt. The heavy flocculent precipitate, which, if the solutions were strong, entirely filled the liquid, and even piled up above its surface, became crystalline on standing, and was purified by washing with cold water. Some of the salt is also formed when argentic nitrate is added to an aqueous solution of the free metabromdinitrophenylacetic acid. The analysis of the salt gave the following results.

0.3530 gr. of the air-dried salt lost, when heated to 100°, 0.0149 gr.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag . H_2O$.	Found.
Water	4.19	4.22

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* Ber. d. ch. G., ii. 210.

† Ibid., xiv. 823.

‡ Ann. Chem., ccxx. 134.

I. 0.1674 gr. of the salt dried at 100° gave, after being heated with fuming nitric acid in a sealed tube * and precipitated with potassic bromide, 0.0761 gr. of argentic bromide.

II. 0.1556 gr. of the salt treated in the same way gave 0.0707 gr. of argentic bromide.

	Calculated for $C_6H_2Br(NO_2)_2CH_2CO_2Ag$.	Found.	
		I.	II.
Silver	26.21	26.11	26.10

Properties. — The argentic bromdinitrophenylacetate forms white flat prisms terminated by a single plane at an oblique angle; the terminated end is somewhat broader than the other, so that the crystals look like a flattened base-ball bat. They have also a tendency to twin longitudinally. When put in the flame of a Bunsen lamp, they burn with a sparkling flame, but when heated carefully on a piece of porcelain, decompose quietly leaving a residue of silver. The substance is very slightly soluble in cold water, so that it can be washed without too great loss; more soluble in hot water, from which it crystallizes apparently without decomposition; insoluble in cold alcohol, but slowly decomposed, if heated with it.

Constitution of Bromdinitrophenylmalonic Ester.

The formation of metabromdinitrotoluol from bromdinitrophenylmalonic ester by a series of reactions giving essentially a quantitative yield and taking place at temperatures not above 150°, throws a great deal of light on the nature of this substance. In the first place, its conversion into a toluol derivative is a welcome confirmation of the formula which we have given it, and which did not rest on the most secure experimental foundations. In our first paper it was stated that the analysis left the choice open between the following formulas,

I. $C_6H_2Br(NO_2)_2CH(COOC_2H_5)_2$,

II. $C_6HBr(NO_2)_2C(COOC_2H_5)_2$,

and we decided in favor of the first on account of the analyses of the sodium salt, an amorphous substance for the purity of which we had no guaranty, and also on account of the ease with which this salt was formed and decomposed, the product of the decomposition being the original ester. Against this formula stood only our inability at the time to explain the reactions by which it was formed, an objection which is removed by this paper. The easy conversion of a substance having Formula I. into a toluol compound is to be expected, whereas with one having Formula II. it would be necessary to add two atoms of hydrogen, an action which could hardly take place quantitatively by boiling with dilute sulphuric acid, or distillation with steam, the two processes employed in converting the bromdinitrophenylmalonic ester into the bromdinitrotoluol. This formation of the substituted toluol therefore establishes Formula I. beyond question.

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* We had hoped in this way to determine both the silver and bromine in one operation, but found that the filtrate gave a precipitate with potassic bromide. It would seem, therefore, that the presence of an excess of argentic nitrate is necessary to retain all the bromine.

In the second place, the way is opened to the determination of the position of the substituting radicals upon the benzol ring in all these compounds, as their position must be the same as in the bromdinitrotoluol. Messrs. W. B. Bentley and W. H. Warren have accordingly, at our request, determined the constitution of the bromdinitrotoluol by replacing its bromine successively by the amido group and by hydrogen, and have found in this way that its constitution is

$$CH_3 . Br . NO_2 . NO_2 . 1 . 3 . 4 . 6.$$

For the details of their work we would refer to their paper, which follows immediately after this. It follows from this that in the tribromdinitrobenzol $Br . H . Br . NO_2 . Br . NO_2 . 1 . 2 . 3 . 4 . 5 . 6$, the bromine numbered 1, which stands in the ortho position to one nitro group and the hydrogen, in the para position to the other nitro group, has been replaced by the malonic ester radical $CH(COOC_2H_5)_2$; that the bromine replaced by hydrogen is the one between the two nitro groups; and that the third bromine, which is in exactly the same relation to the nitro groups as the one replaced by the malonic ester radical, is left entirely unaltered. This last fact seems very strange to us. The constitution of our bromdinitrophenylmalonic ester is therefore represented by the following graphical formula: —